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From the Organic Chemistry Laboratory of the
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SYNTHESES USING ACETYLENE
(Preliminary Report)

A. Ye. Chichibabina

ABSTRACT

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A summary is given of past experiments on acetylene condensation reactions. In his own experiments the author finds that acetylene can be formed during various types of acetaldehyde condensation from acetylene by eliminating water. It is found that acetylene condensation reactions and acetaldehyde condensation reactions are very similar.

Author

The foundation of the study of acetylene condensation reactions, /703* as is well known, was laid in 1866 by the famous papers of Berthelot[1], who derived benzene from acetylene at high temperature, and later a whole series of aromatic hydrocarbons as well. In recent years, this reaction has been reproduced on a large scale by R. Meyer[2], who brought

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* Note: Numbers in the margin indicate pagination in the original foreign text.

[1] C. R., 62, 905; 63, 479, 515 (1866); A. chim. (4), 9, 445 (1866); 12, 52, 64 (1867); 16, 143, 172 (1869), and so on.

[2] Ber., 45, 1609 (1912). Compare also C. R., 130, 1319 (1900); Brodley, Jacobs. D. R. P., 125-936 [Cbl. (1902), 77].

about condensation of acetylene in a hydrogen mixture at 640°-650°, during which the reaction products were studied in great detail.

Somewhat later, specifically in 1877, Ramsay[1] and Dewar[2] began to investigate condensations leading to the formation of the simplest heterocyclic compounds. Dewar, by passing a mixture of acetylene and ammonia through incandescent tubes, was at times successful in producing traces of pyrrole in addition to ammonium cyanide. By passing /704 a mixture of acetylene and hydrocyanic acid through an incandescent tube, Ramsay produced traces of pyridine. Although N. N. Lyubavin[3] was unsuccessful in corroborating Ramsay's observation, this reaction has now already been reproduced in more significant amounts by R. Meyer[4]. If methane is present in addition to acetylene, a mixture of pyridine bases is obtained, which the authors were unable to separate.

W. Meyer and Sandemeir[5] produced a slight amount of thiophene by passing acetylene through heated sulfur. This reaction was later perfected by Steinkopf and Kirchhoff[6], who used pyrite instead of sulfur on the assumption that the sulfur at the moment of separation would react more mildly than free sulfur. In fact, the thiophene-forming

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[1] Jahresber. 1877, 436.

[2] Jahresber. 1877, 445.

[3] Ber., 18. Ref. 431 (1885). Zhurnal Russkogo Khimicheskogo Obshchestva, 17, 250 (1885).

[4] R. Meyer. Ber., 46, 3183 (1913).

[5] Ber., 16, 2176 (1883).

[6] Lieb. Ann., 403, 1 (1913.

reaction under these conditions begins at as low a temperature as 260°. Despite this reduced reaction temperature, the authors insist that catalysis does not occur here, since neither natural marcasite nor pyrite - made artificially from ferrous sulfide and sulfur - exerts the same effect. The authors evidently by no means think that not only pyrite admixtures, but also the pyrite itself or ferrous sulfide, can catalyze the reaction with sulfur, although their experiments show that ferrous sulfide itself does not condense acetylene, or merely does so in an insignificant amount (without sulfur).

Comparatively recently cases have been discovered of the catalytic influence of acetylene on condensation reactions.

First of all, Moissan and Mouret[1] found that, in the presence of platinum and pyrophoric iron, acetylene condenses into benzene even at an ordinary temperature and partially breaks down into carbon and oxygen.

Then Erdman' and Ketner'[2] observed that, during the passage of acetylene through heated cuprous oxide, a cork-like mass of hydrocarbons /705 is produced in addition to other products[3]. A similar light-brown cork-like hydrocarbon is also obtained when acetylene is passed through finely comminuted copper at 240°-250°[4]. According to Sabatier[5], this mass consists of a high-molecular hydrocarbon of formula $(C_7H_6)_x$, which he

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[1] C. R., 122, 1240 (1896); Bl. (3), 15, 1296 (1896).

[2] Zeit. angew. Chem., 18, 49 (1898).

[3] See also Goach., Baldwin. Zeit. angew. Chem., 22, 235 (1900).

[4] Alexander. Ber., 32, 238 (1899).

[5] C. R., 130, 250 (1900).

calls cuprene, and containes a further admixture of copper, as well as other high-molecular compounds.

Subsequently, Sabatier and Senderens[1] found that finely-comminuted nickel exerts the same effect on acetylene at temperatures above 180°. At even lower temperatures (100°-150°), a colorless liquid[2] - smelling of kerosene and proving to be a mixture of methane, ethylene, and aromatic hydrocarbons - is produced in addition to ethylene and ethane. The same results were obtained with copper[3] and platinum[4]. Cobalt also displays action between iron and nickel[5].

In all of these catalytic reactions, three main processes are occurring side by side:

(1) Local breakdown of acetylene into carbon and hydrogen, accompanied by polymerization into aromatic hydrocarbons.

(2) Condensation into a solid hydrocarbon, like cuprene.

(3) Hydrogenation of acetylene and aromatic hydrocarbons, during which paraffin, ethylene, and cyclic hydrocarbons are produced.

In general, all the reactions do not take place smoothly and, according to Sabatier, are accompanied by further splitting of the hydrocarbon molecules into residues of CH_3, CH_2, and CH which inter-

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[1] C. R., 131, 187 (1900).

[2] C. R., 128, 1173 (1899).

[3] C. R., 130, 1559 (1900).

[4] C. R., 131, 46 (1900).

[5] Sabatier, Senderens. An. chim. (8), 4, 430 (1905). Sabatier and Senderens also obtained similar results with ethylene (C. R., 131, 267 (1900).

combine in the most varied ways[1].

By varying the conditions, Sabatier and Senderens managed to derive from acetylene a hydrocarbon mixture similar to Pennsylvania petroleum (with excess hydrogen), Caucasian petroleum (of acetylene without admixture of hydrogen), and intermediate varieties of petroleum /706 (Galician, Romanian, etc.). This occasioned their theory of petroleum formation from acetylene in the presence of metals[2].

It is interesting that Sabatier is inclined to attribute the presence of nitrous compounds in petroleum, and also the optical behavior of petroleum, to admixtures of substances having an organic origin.

From the above, it is evident that the catalytic effect of metals has already been studied in substantial measure with respect to the condensation reactions of acetylene, but with regard to oxides there are only data on cuprous oxide.

Some years ago V. N. Ipat'yev[3] demonstrated that at high temperatures and pressure, ethylene can produce solidified products, while aluminum oxide affects the reaction speed. Ipat'yev was unsuccessful in polymerizing ethylene at atmospheric pressure.

In an article on the origin of petroleum[4], Ipat'yev points out that his experience with the condensation of ethylene might be inter-

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[1] Sabatier, La catalyse en chimie organique, Paris - Liege. 1913, pp. 156 and 99.

[2] C. R., 128, 1173 (1899); 131, 267 (1900). Rev. d. M. II, 257 (1907). Sabatier, La catalyse, p. 99.

[3] Zhurnal Russkogo Khimicheskogo Obshchestva, 43, 1420 (1911). See also Engler, Ber., 42, 4620 (1909).

[4] Zhurnal Russkogo Khimicheskogo Obshchestva, 43, 1737 (1911).

preted as pointing to the hypothesis of the mineral origin of petroleum, but he advises not to get carried away by the possibility of chemical reactions leading to the formation of petroleum-like mixtures. Instead, he favors the organic theory of petroleum.

It seemed to me that a study of the catalytic effects during condensation of ethylene and acetylene hydrocarbons deserved even more attention than it has been given up till now. A particularly important gap, in my opinion, was the lack of attempts to apply catalysts to the condensation of hydrocarbons with metalloids and their simplest (especially hydrocarbon) compounds, and then also even with more complex organic compounds of the same metalloids.

Such experiments were initiated about two years ago in the Organic Chemistry Laboratory of the Moscow Technical College, and from the very beginning, these experiments have given a number of very interesting results.

As catalysts, I chiefly tested not metals, but metal oxides, /707 and, in part, metal salts, since the experimental results presented above of other investigators indicate the great complexity of reactions which acetylene undergoes when acted upon by metals. As has already been indicated above, the study of the effect of oxides on acetylene condensation can be regarded as having barely begun. The interesting experiments of V. N. Ipat'yev on condensing ethylene by means of aluminum oxide at high pressure led one to expect that for acetylene - whose carbon atoms are far less saturated than in ethylene - the condensation

reactions would take place comparatively readily even at ordinary pressure.

Experiments have fully confirmed this supposition. In fact, acetylene condensation reactions proceed in the presence of some oxides even at relatively low temperatures. The principal oxides tested were those of triatomic metals, $A\ell_2O_3$, Fe_2O_3, and Cr_2O_3. The first reaction, in which the experiment immediately showed the correctness of the leading idea presented above, was that of acetylene with ammonia in the presence of aluminum oxide.

Further research into this reaction was conducted with the aid of P. A. Moshkin, a student at the Technical College. Up until now, this research has led to the following results:

When acetylene and gaseous ammonia are passed through tubes containing the above oxides, a reaction occurs between the acetylene and ammonia even at temperatures slightly higher than 300°. The lower temperature limit at which the reaction still takes place has not as yet been established.

The reaction produces a liquid condensate which begins to boil at temperatures above 100° and has wide boiling point limits; however, after fractionation most of the condensate boils between 125° and 145°. A more detailed study of the condensate has enabled us to establish the following facts.

(1) Pyridine bases comprise the bulk of the product.

(2) Among these bases, the vast majority have the formula C_6H_7N, i.e., they are picolines, and, specifically, almost equal quantities of

α-picoline and γ-picoline are obtained. The mixture contains no β-picoline.

(3) Attempts to find pyridine itself in the mixture gave negative results, and we may confidently assert that the condensate contains no /708 pyridine.

(4) From the above pyridine homologs, a rather large quantity of collidines is produced. We have been successful in determining the presence of aldehydine in the mixture, i.e., α-methyl - β-ethylpyridine, by using a picrate.

(5) Apparently the mixture contains no lutidines at all.

(6) The condensate also contains rather considerable amounts (several percent) of pyrrole.

(7) In addition, the condensate contains a few secondary bases - which are apparently piperidine bases - as well as a few neutral products.

(8) Rather substantial amounts of hydrogen gas are formed during the reaction.

Therefore, all the products discovered contain an even number of carbon atoms, i.e., under the experimental conditions the acetylene molecules do not split, and the three following types of condensation are established:

I $2C_2H_2 + NH_3 = C_4H_5N$ (pyrrole) $+ H_2$,

II $3C_2H_2 + NH_3 = C_6H_7N$ (picolines) $+ H_2$,

III $4C_2H_2 + NH_3 = C_8H_{11}N$ (collidines).

The first reaction was discovered long ago by Dewar. However, he

conducted the reaction at very high temperatures, when the acetylene molecule in splitting gave ammonium cyanide as its main nitrogenous product[1]. No one has yet observed the other two types of reaction for acetylene.

The composition of the condensate changes quantitatively somewhat, depending on the catalyst. Thus, more pyrrole is formed if the catalyst used is ferric oxide, rather than aluminum oxide.

Similar condensates were also obtained with oxides of tetratomic elements, e.g., with titanium oxide, thorium oxide (containing less silica), as well as with several salts of triatomic metals, e.g., with aluminum phosphate, kaolin, etc., at somewhat higher temperatures.

It seemed very interesting to ascertain whether ethylene would also enter into reaction under similar conditions. The experiments /709 which were conducted showed that a condensate could also be obtained from ethylene which contained pyridine bases, but that this required a higher temperature. It is probable that ethylene changes with the formation of acetylene[2], and that this acetylene enters into the reaction. The composition of the condensates from ethylene has not yet been investigated.

In view of the success of experiments with ammonia, it was very interesting to test the application of the same catalysts also to other types of condensation, and principally their application in the

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[1] In our experiments no ammonium cyanide is formed at all.

[2] See below. Chem. Ztg. Report. 1894, 89.

production of thiophene. Experiments in this direction were conducted with the participation of O. Bagdosor'yants, a student in the Technical College. Aluminum oxide was almost exclusively used as the catalyst. Acetylene and hydrogen sulfide were brought into the reaction, but condensation also proceeds with sulfur vapors.

The experiment showed that in this case condensation takes place readily even at comparatively lower temperatures, although comparatively rapid condensation requires somewhat higher temperatures than in the experiments of Steinkopf and Kirchhoff with pyrite. The reaction here leads to the formation of thiophene, which is the overwhelmingly preponderant product and which is consequently formed in accord with the equation

$$2\ C_2H_2 + H_2S = C_4H_4S + H_2.$$

Moreover, products with high boiling point are also derived, which consist principally of thiophene homologs, as is shown by color reactions and by the capability of producing mercury derivatives, from which thiophene homologs may be re-obtained by boiling with acids. Judging from the boiling point of the fraction following the thiophene fraction, no compounds are formed with an odd number of carbon atoms in the molecule, and the nearest homolog is apparently ethylthiophene.

The reaction described can be a very convenient method of producing thiophene on a large scale. It is even more convenient than Steinkopf and Kirchhoff's method, since a comparison of both products showed that the raw thiophene derived with aluminum oxide is much purer, and moreover, the acetylene does not carbonize to any con-

siderable degree, as occurs to a great extent under Steinkopf and Kirchhoff's conditions.

In opposition to the opinion of these authors, I assume that in their experiments a catalytic process occurs, in which the catalyst /710 is the pyrite itself and iron monosulfide, or only one of these substances.

It was interesting to find out whether water gave a reaction such as that with hydrogen sulfide and ammonia, and whether it would consequently result in the formation of furan:

$$2\ C_2H_2 + H_2O = C_4H_4O + H_2.$$

Actually, the passage of acetylene and steam through aluminum oxide at 400°-425° produced a condensate in which a qualitative reaction (green coloration of chips impregnated with hydrochloric acid and dried) revealed the presence of furan.

The condensation of dry acetylene has been investigated comparatively recently. When acetylene is passed through heated aluminum oxide beginning at a temperature below 400°, a liquid condensate is obtained which consists mainly of unsaturated and aromatic hydrocarbons. Benzene is found in the condensate, although in an amount of less than 10% of the total liquid product. Preliminary study indicates that the composition of the condensate obtained differs from that of the condensate in the experiments of Berthelot and Richard Meyer due to the substantial content of unsaturated hydrocarbons, and also evidently in its lack of hydrocarbons with an odd number of carbon atoms in the molecule. At present, a detailed study of the condensate has already

been initiated.

When condensing acetylene with ammonia through heated aluminum oxide, we in some cases noted that a small number of crystals were separated out. These crystals were segregated and studied; it was found that the crystalline substance was nothing else but aldehyde ammonia. This could be formed from acetylene by the combination of water and ammonia. As is known, thirty-five years ago Kucherov established that acetylene is capable of joining with water and giving aldehyde under the influence of mercuric oxide salts[1].

The formation of aldehyde ammonia from acetylene under the conditions of my experiments led me to the assumption that in these cases the first reaction is the attachment of water to acetylene and the formation of acetaldehyde. The latter enters into the condensation reaction and splits off water, which then again combines with the acetylene, and so on. According to this supposition, the traces of water, which it is impossible to avoid, would also play the role of catalyst. /711

Such an assumption coincides with the results of my experiments, which showed that when moist acetylene and ammonia are passed through heated tubes filled with heavy metal oxides of the RO type - as, for instance, FeO, ZnO, NiO - aldehyde ammonia is obtained as the main product. Passing moist acetylene without ammonia through the same oxide produces a liquid product in which - in addition to substances with high

[1] Strangely this reaction has now been the subject of a German patent issued to the Grünstein firm of Frankfurt-am-Main. See Cbl. 1914, I, 716.

boiling point - acetaldehyde and crotonaldehyde have been detected.

On the other hand, on the basis of the above assumption regarding the mechanism of the condensation reaction, it was to be expected that acetaldehyde could give all the condensation reactions which were discovered for acetylene.

With respect to the condensation of aldehydes and ammonia, P. S. Panyutin, a student at the Technical College, and I had already earlier conducted a series of experiments[1] which determined that, when aldehydes and ammonia are passed through aluminum oxide at temperatures above 300°, all those pyridine bases may be produced which formerly were derived by various investigators using the reaction of aldehyde with ammonia under other conditions[2]. In addition, a new type of aldehyde and ammonia condensation was established, which leads to the formation of pyridine homologs with the side chain in the γ-position.

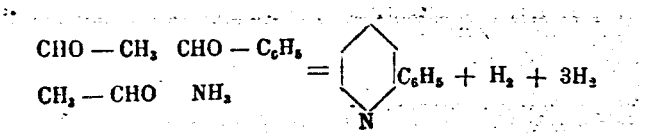
Thus, for example, when ammonia and a mixture of acetaldehyde and benzaldehyde is passed through aluminum oxide heated to 360°, α-phenyl pyridine is also obtained in addition to γ-phenyl pyridine.

The formation of α-phenyl pyridine may be expressed by the /712

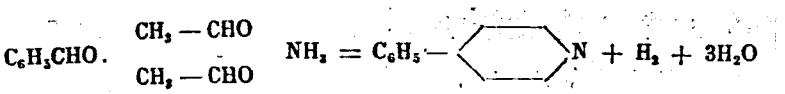
[1] Reported at a session of the chemistry section of the Moscow Society of Amateurs of Nature, Anthropology, and Ethnology, December 11, 1913, and soon to be published as a separate article.

[2] Compare A. Chichibabin, "Methods of Synthesizing Pyridine Bases from Aldehydes and Ammonia, Zhurnal Russkogo Khimicheskogo Obshchestva, Vol. 37, 1905, p. 1229.

equation:

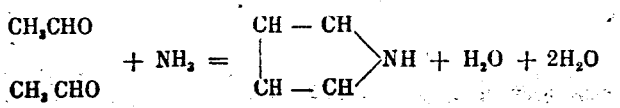


while the formation of γ-phenyl pyridine corresponds to the equation:



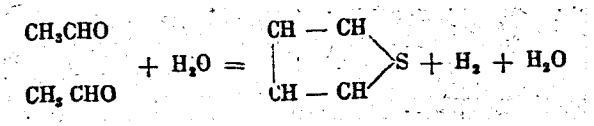
Out of the above condensation products of acetylene with ammonia, two - α-picoline and aldehydine - have already been previously discovered as the condensation products of acetaldehyde and ammonia.

I have now established that when acetaldehyde and ammonia are passed through heated aluminum oxide, in addition to other products, pyrrole is obtained, which is formed according to

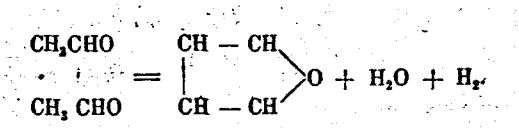


On the other hand, the experiment of passing acetylene, ammonia, and benzaldehyde vapors through a tube of aluminum oxide at 350°-420° showed that here, too, a mixture of α- and γ-phenyl pyridines was derived in addition to other products.

In addition, I also discovered that, when a mixture of acetaldehyde (or paraldehyde) vapors and hydrogen sulfide is passed through heated aluminum oxide, a rather considerable quantity of thiophene can be produced in accord with the equation



Finally, a series of experiments in passing acetaldehyde (or paraldehyde) vapors alone through aluminum oxide and other oxides of triatomic or tetratomic metals[1] showed that - in addition to other /713 condensation products (crotonaldehyde and obviously other hydrocarbons)[2] - significant amounts of furan and its homologs are produced. Furan is formed in conformity with the equation



Whether or not acetaldehyde - in accord with the above assumption - is in fact the first product formed from acetylene under the influence of metallic oxides, or vice versa, it should be recognized that acetylene can be formed in the various types of acetaldehyde condensation from acetylene by eliminating water. In any case, the above-described experiments may be considered to have completely proven the great similarity between acetylene condensation reactions, on the one hand, and acetaldehyde condensation reactions, on the other. This enables one to assume that in other cases, where acetaldehyde partici-

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[1] These experiments are in inexplicable contradiction to those of V. N. Ipat'yev (Zhurnal Russkogo Khimicheskogo Obshchestva, Vol. 38, 1906, p. 92), who stated that in passing through aluminum oxide at 420°-480°, acetaldehyde changes hardly at all and merely polymerizes into paraldehyde.

[2] They have been left out of consideration in previous experiments. Meanwhile, it would be very interesting to find whether benzene is present or absent. These experiments will soon be set up.

pates in the reaction, the same products may also in many cases be derived from acetylene in the presence of the appropriate metallic oxides.

The following experiment has been undertaken in this direction. According to the well-known Döbner-Miller reaction, acetaldehyde and anilide give α-methyl quinoline (quinaldine). The experiment I performed in passing acetylene and aniline vapors through aluminum oxide at 360°-420° gave indole, among other products, as well as quinoline homologs - although a preponderant amount of lepidine (γ-methyl quinoline), and not quinaldine, was obtained. Careful analysis of the Döbner-Miller reaction product showed me that this reaction can produce a small quantity of lepidine, in addition to quinaldine.

Together with students in the organic chemistry laboratories of the Moscow Technical College and Shanyavskiy University, I am conducting a detailed investigation of most of the above-described reactions. A portion of this investigation has already been concluded, and will be published in detail in the immediate future.

January 27, 1915.

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